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STRUCTURE AND THERMODYNAMIC MELTING PARAMETERS OF WHEAT STARCHES WITH DIFFERENT AMYLOSE CONTENT

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Abstract

The hierarchical granule structure of starches with different amylose content extracted from winter wheat was investigated using light microscopy (LM), scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXS), high-sensitivity differential scanning calorimetry (HS DSC) and different thermodynamic approaches. Morphology (size, size distribution and shape), crystallinity of native granules with different amylose content (1.5–39.5%), as well as the cooperative melting unit, thickness of crystalline lamellae, heat capacity drop related to hydration during melting of native granules, and thermodynamic parameters related to the surface of crystalline lamellae were determined. The relationship between structure and thermodynamic properties of mutant wheat starches is discussed.

Keywords: amylose, mutant wheat, starches, thermodynamic melting parameters

Introduction

The amylose/amylopectin ratio spans a wide range of values in starches of mutant lines of crops like maize, pea, barley, sorghum, potato and rice. For example, the amylose content in maize and pea starches ranges from 0 to 84% [1–3], while in barley starches it usually does not exceed 43% [4]. Recently the wheat starches with an amylose content ranging from 0.2 to 50% have been selected in Japan, USA, Canada and Russia [5–10]. In Russian varieties of winter wheat, the content of amylose varies from 19 to 50% [10].

Taking into consideration that (*i*) within the last decade, wheat starch production increased considerably [11], (*ii*) in the years 1998–2000, the starch from normal wheat accounted for the 29–32% of the total starch production [12, 13], (*iii*) mutant

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maize starches are widely used in different branches of industry [12] since their functional properties can be tuned according to differences in amylose/amylopectin ratio [2], it seems a reasonable expectation that an increased production of special starches may come from a suitable mutant wheat, selected within the traditional European crops.

To this aim, the relationships between structure and thermodynamic and functional properties have to be assessed, since they still are poorly studied for starches from mutant wheat. The relevant data published so far are limited to the study of starches with an amylose content ranging from 0.2 to 28%. It was shown that:

i) the molecular weight of amylopectin was negatively correlated with the amylose content in wheat starches where this was between 26.6 and 0.2% [8];

ii) the polymorphous structure of mutant wheat starches was of the *A*-type, i.e. the same as for starches extracted from normal and wild wheat [7];

iii) the highest crystallinity was detected for waxy wheat starch [14];

iv) waxy, partially waxy and wild wheat showed significant differences in onset and peak transition temperatures as determined by DSC [5, 14];

v) waxy wheat starch had higher enthalpy than normal wheat starch [5, 14].

Taking into consideration that starch granule is a complex hierarchical structure consisting of polysaccharide macromolecules partially arranged in ordered conformations (double and single helixes) and entangled to form supra- and sub-molecular structures, the relationship between structure and thermodynamic properties of starches can be found at different levels of the structural organization.

It is known that amylopectin and amylose macromolecules play different roles in the structural organization of native granules. The granules consist of crystalline lamellae with a thickness of 4–6 nm mostly formed by double helixes of amylopectin *A*-chains, amorphous lamellae formed by amylopectin *B*-chains, and an amorphous matrix formed by amylopectin and amylose macromolecules in a random conformation [21, 22]. In the case of cereal starches, a minor portion of amylose forms complexes with lipids, which can be either amorphous or arranged in a single helix conformation and ordered in a *V*-type crystal structure [21, 22]. Moreover, amylopectin and amylose macromolecules, within the either amorphous or crystalline lamellae, can form defects like molecular ordered structures and tie-chains [21, 23]. An accumulation of defects is observed during the biosynthesis and depends on the environmental conditions [18, 24–27].

As for the calorimetric evidence, the current interpretations are:

(*i*) the width of calorimetric melting peaks is a function of the size distribution of native granules [28];

(*ii*) the melting temperature is a function of the starch polymorphous structure, thickness of crystalline lamellae and surface free energy of crystal face. The main contribution to the surface free energy of crystal face is of entropic nature and is proportional to the concentration of the structure defects [24–27];

(*iii*) the value of the melting enthalpy is proportional to the starch crystallinity.

Reasonable relationships between structural parameters and thermodynamic and functional properties were so far suggested for maize and pea starches. However, even for these starches, literature reports different points of view. For example, according to Zobel [15], high amylose starches adopt the *B*-type structure, while Gernat *et al.* [16] claim that wrinkled pea and amylomaize starches contain both *B*- and V_h-type crystal structures. Gerard *et al*. [17] stated that high amylose maize starches can contain *C*-type structures. Recently high amylose pea and maize starches were reported to contain both *B*- and *B**-type structures with different length of the double helixes [18, 19]. It was also found that waxy, normal and high amylose barley starch have the same *A*-type structure [20]. In the light of the above discrepancies, the direct use of the already existing information about ‘traditional’ starches from different crops and, above all, from the not enough known mutant wheats, may be rather unreliable.

The aim of this work is to answer some of the questions listed above for mutant wheat starch with different amylose content. Different physical and chemical approaches usually applied for studying structural features of synthetic polymers and starches, as well as structural data obtained by means of optical and scanning electron microscopy, and X-ray diffraction, were used to clarify some assumptions.

Experimental

Materials

Different wheat varieties were selected by means of chemical mutagenesis, using ethylene-imine as a mutagen, with the exception of Moscovskaja-39’s wheat which was selected by traditional breading. The line, obtained in three generations, namely: Beseda, Botovskaya, imeni (im) Rapoporta, Ritza and Bulova, was the basis for investigated varieties. The wheats investigated were grown in Central Russia (Moscow’s Region) in the 2000-season.

Table 1 Degree of crystallinity, cooperative melting unit (ν) and thickness of crystalline lamellae in wheat starches with different amylose content

Wheat varieties	Amylose content/%	Degree of crystallinity/%	ν, anhydroglucose residues	L_{crl}/nm
Leona	1.5	30	12.7±0.2	4.5±0.4
Beseda	11.2	25	12.4±0.4	4.5±0.2
Moskovskya-39	21.0	–	12.9±0.8	4.6±0.2
Botovskaya	21.5	–	12.5±0.4	4.5±0.3
im. Rapoporta	26.0	–	13.9±0.4	4.9±0.2
Ritza	26.5	25	13.0±0.4	4.6±0.2
Bulava	39.5	23	12.1±0.7	4.2±0.2
Mean			13.3±1.6	4.7±0.5

Native starches were isolated according to Richter *et al*. [29]. The starch from Leona's wheat variety was kindly supplied by Dr. P. Seib.

The amylose content in starch samples was determined using a method described previously [29]; the relevant values are shown in Table 1.

Methods

Light microscopy (LM)

Analyzed starches (0.8 g) were re-suspended in MQ (de-ionized) water (10 mL) and were heated for 15 min at a proper temperature selected according to the DSC results (peak temperature). For Bulova and Leona starches, beside the respective peak temperatures 56.7, 62.0 and 75.0°C was considered as an additional temperature.

The obtained 8% starch pastes were smeared over a microscopy glass and stained with iodine after cooling. The samples were covered with another glass and observed in an LM microscope OLYMPUS BX60.

Scanning electron microscopy (SEM)

Starch granule morphology was studied with SEM. Starches were deposited onto a copper disc and coated with gold using a Jeol JEE-400 vacuum evaporator. The specimens were examined in a scanning electron microscope Jeol 5200 at 5 kV accelerating voltage.

Size distribution of granules

The size distribution of starch granules was assessed using a granulometer GIY-1 which works as a computer processor of light microscopy data. Starch granules were approximated by spheres.

X-ray diffraction

Wide-angle X-ray scattering (WAXS) measurements of starch powders were carried out with a diffractometer equipped with one-dimensional position-sensitive detector [30] built in JINR (Dubna, Russia). WAXS patterns were recorded in transmission geometry with CuK$_\alpha$ radiation and plotted as intensity, $I(S)$ *vs*. $S=(2\sin\theta)/\lambda$, where λ is CuK$_\alpha$-wavelength (0.1542 nm) and θ is half of the scattering angle.

The crystallinity (C) of a given starch, i.e. the mass fraction of its crystal phases was assessed on the basis of the X-ray absorbance coefficient $K=I_0/I_t$, where I_0 and I_t are the intensity of incident and transmitted X-ray beam, respectively. Account was taken of the background scattering $I_b(S)$, recorded from the empty sample holder, and of the WAXS pattern of 'amorphous' (6-hour dry-milled) wheat starch, in order to obtain the normalized WAXS pattern $I_{norm}(S)$ which was referred to the unit sample mass:

$$I_{norm}(S)=[I(S)K-I_b(S)](\ln K)^{-1} \tag{1}$$

The crystallinity of the starch samples was evaluated as

$$C=(1-k)100\% \tag{2}$$

where k is an empirical factor that made the normalized WAXS pattern of ‘amorphous’ starch to closely approach the WAXS pattern of the analyzed starch in the vicinity of $S\approx1.5\ \mathrm{nm}^{-1}$ and $S\approx2.4\ \mathrm{nm}^{-1}$. An example of such fitting is shown for one starch sample in Fig. 1.

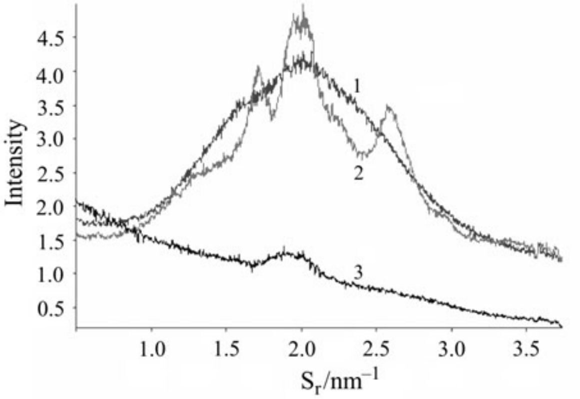


Fig. 1 Experimental X-ray diffraction patterns of: 1 – amorphous (6-hours dry-milled native wheat starch) wheat starch, 2 – native wheat starch of Beseda variety and 3 – background from the empty pan

High-sensitivity differential scanning microcalorimetry

Calorimetric investigations of aqueous starch dispersions (0.3–0.5% dry matter, sample volume 0.5 cm^3 in sealed cells) were performed using a high sensitivity differential scanning microcalorimeter DASM-4 (Puschino, Russia) in the 10–120°C temperature range with a 2 $\mathrm{K\ min}^{-1}$ heating rate and 2.5 bar excess pressure. MQ water was used as a reference material. The heat capacity scale was calibrated using the Joule-Lenz effect for each run. Corrections for dynamic lag and residence of the samples in calorimetric cell were not necessary under the conditions used [31, 32].

The average values of the thermodynamic parameters were determined as described elsewhere [19, 31, 32], using five measurements at 95% significance level, and converted into per mole of anhydroglucose units (162 $\mathrm{g\ mol}^{-1}$).

vant Hoff’s enthalpy (ΔH^{vH}) values were calculated according to [19, 31–33].

For starches which gave a symmetric DSC signal, a previously reported method [19, 24, 26, 27, 31, 32] was used to evaluate the melting cooperative unit, ν,

$$\nu=(\Delta H^{\mathrm{vH}})/(\Delta H_{\mathrm{m}}) \tag{3}$$

where ΔH_{m} is the experimental melting enthalpy of crystalline lamellae, and the critical thickness of crystalline lamellae, L_{crl},

$$L_{\mathrm{crl}}=0.35\nu \tag{4}$$

that, according to [34], corresponds to a pitch height of 0.35 nm per anhydroglucose residue in the double helix.

The thermodynamic parameters relevant to the surface of the crystalline lamellae were evaluated applying the Thomson–Gibbs' equation (5) to the symmetrical DSC melting signals [24–27, 35]:

$$T_m = T_m^0[1-2\gamma_i/(\Delta H_m^0 \rho_{crl} L_{crl})] \qquad (5)$$

and using the other expressions,

$$q_i = [(\Delta H_m^0 - \Delta H_{exp})L_{crl}]/2.5 \qquad (6)$$

$$\gamma_i = q_i - T_m s_i \qquad (7)$$

where T_m^0 and ΔH_m^0 are the melting temperature and the melting enthalpy, respectively, of a hypothetical crystal with unlimited size (a perfect crystal); ρ_{crl} and L_{crl} are the density and the thickness of the crystalline lamellae; γ_i, q_i and s_i are the relevant surface free energy, enthalpy and entropy, respectively; ΔH_{exp} is the experimental enthalpy.

The T_m^0 and ΔH_m^0 values were approximated with those relevant to *A*-type spherulitic crystals, namely, T_m^0=366.5 K and ΔH_m^0=35.5 J g^{-1} [36], and the value of ρ_{crl} with that of *A*-type structures, namely, 1.48 g cm^{-3} [36]. L_{crl}, ΔH_m and T_m were directly evaluated from the experimental DSC traces obtained for the starches investigated.

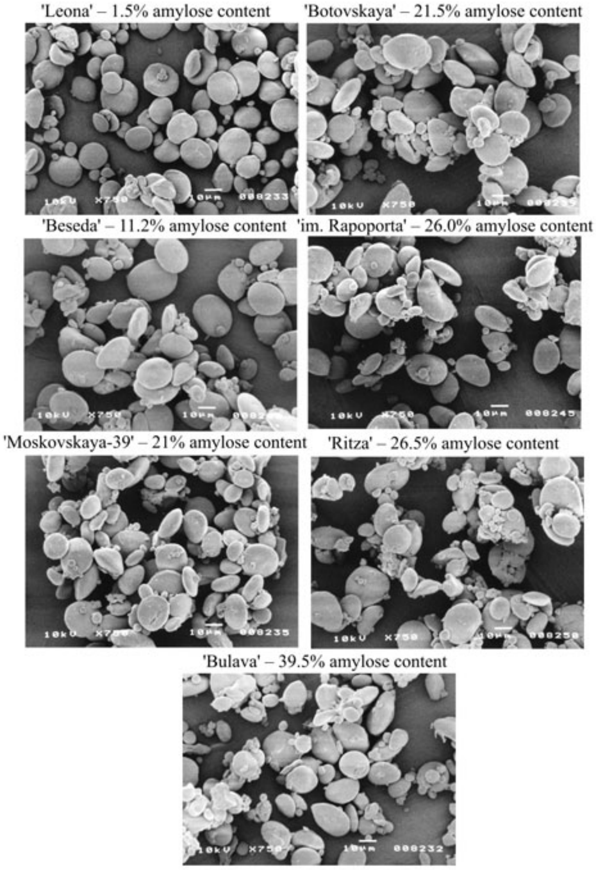
The heat capacity drop related to starch hydration (ΔC_p^{hydr}) and observed across the melting DSC signal of native starches was evaluated according to [21, 23],

$$\Delta C_p^{hydr} = \Delta C_p^{exp} - \Delta C_p^{gtr} \qquad (8)$$

where ΔC_p^{exp} and ΔC_p^{gtr} are the experimentally determined heat capacity drop across the melting signal of native starches and the heat capacity drop related to the glass-to-rubber transition, respectively. According to [21, 23], the ΔC_p^{gtr} value is 12.5±2.8 J mol^{-1} K^{-1}, irrespective of the starch polymorphous structure and origin.

Results and discussion

Scanning electron micrographs of starch granules with different amylose content, extracted from different varieties of wheat, are shown in Fig. 2. These micrographs show that, irrespective of variety and amylose content, the wheat starches have irregularly shaped granules with a relatively smooth surface. Typically the granules were spherical, disc-like or lens-shaped. The size distribution of the granules for all investigated starches is bimodal as far as there are both large and very small granules, which can be referred to as to *A*- and *B*-type. The particle size distribution of wheat starches is shown in Fig. 3. The size of the small granules is below 10–14 μm, the largest fraction being of approximately of 4–6 μm. The size of the large granules ranges between 10 μm and 35–36 μm, the largest fraction being of approximately of 22–28 μm, excepting Leona variety for which a main size of 16–18 μm was found. These results are in agreement with the data relevant to starches extracted from other cereals [37, 38], namely: normal rye and wheat, as well as waxy, normal and high amylose barley, although the fraction of large granules is very high in these cereals.



'Leona' – 1.5% amylose content
'Botovskaya' – 21.5% amylose content
'Beseda' – 11.2% amylose content
'im. Rapoporta' – 26.0% amylose content
'Moskovskaya-39' – 21% amylose content
'Ritza' – 26.5% amylose content
'Bulava' – 39.5% amylose content

Fig. 2 Scanning electron micrographs of native starches with different amylose content, extracted from different wheat varieties

For maize and pea starches an increase of amylose content in granules is accompanied by a transformation of their crystalline lattice. Therefore it could be expected that an increase of amylose content, i.e. passing from amylopectin to high amylose wheat starches, could be accompanied by changes in their polymorphous structure. However X-ray diffraction studies on wheat starches showed that the ratio of crystalline reflexes in the diffractograms and their position (Fig. 4) are always typical of *A*-type starches, irrespective of the amylose content. In other words, the *A*-type polymorphous structure remains unchanged. The same was observed in amylopectin (waxy), normal and high amylose barley starches [20], and and normal wheat starches [7]. Taking into account these apparently opposite behaviours (maize and pea *vs.* wheat and barley), a reasonable conclusion could be that passing from low to high amylose content does not always imply the change in the crystal pattern of starch. Additionally it can be supposed that a subdivision of starches on low and high amylose one characterizes only the deviation in the amylose content in comparison to starches extracted from corresponding

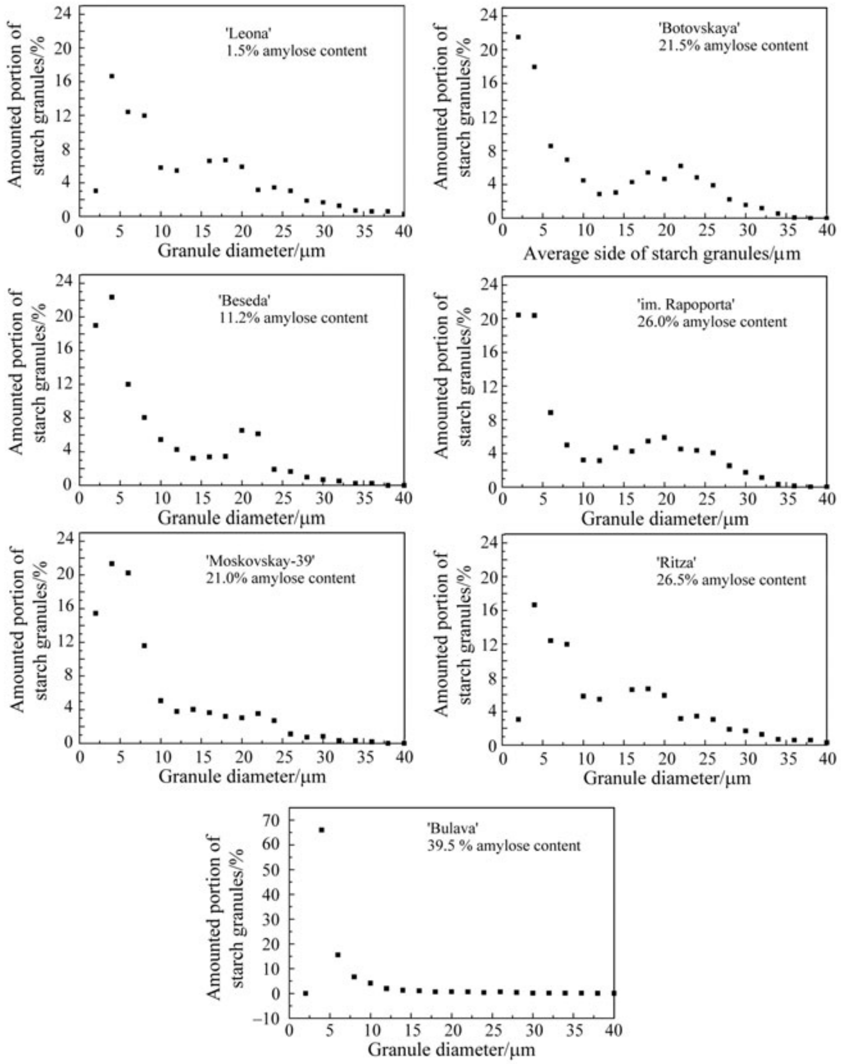


Fig. 3 Granule size distribution of native starches extracted from different wheat varieties

wild plant. It is worth stressing that the changes in polymorphous structure of starches were not always observed.

The calculated degree of crystallinity decreased with increasing the amylose content for four wheat starches containing 1.5, 11.2, 26.5 and 39.5% amylose (Table 1). These results are in agreement with those for starches from waxy and normal wheat as well as from waxy and high amylose maize [7, 19], although the crystallinity of maize starches shows a sharper decreasing trend with increasing amylose content [19].

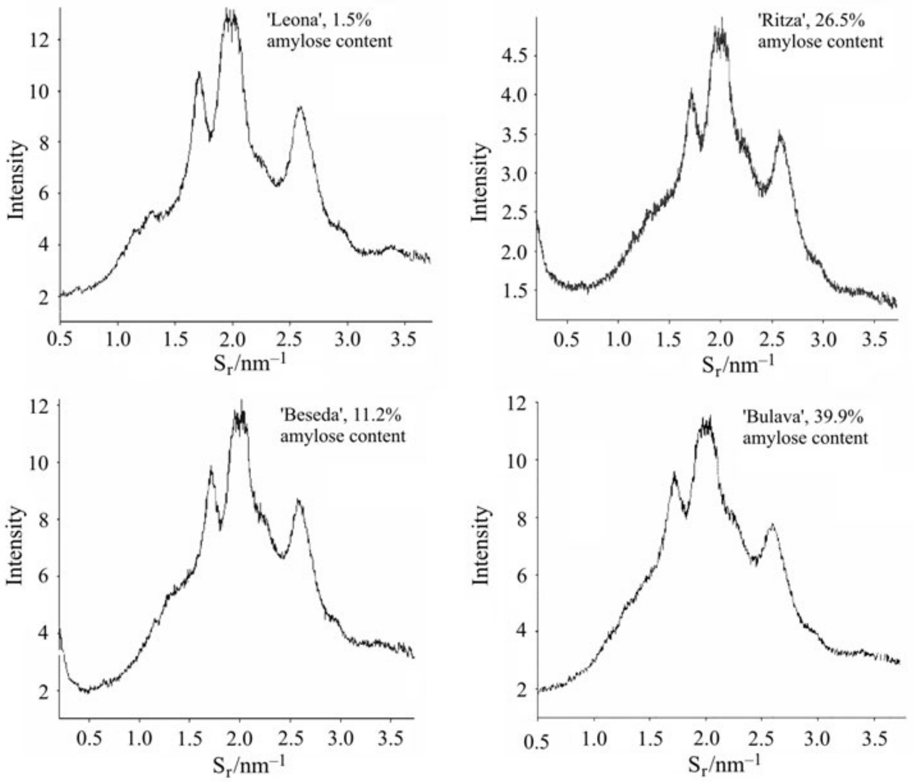


Fig. 4 Normalized X-ray diffraction pattern of native starches extracted from different varieties of wheat

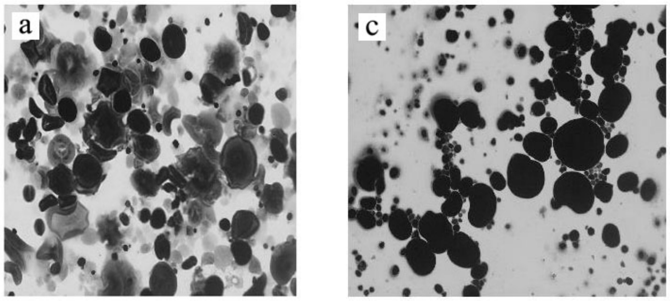
It is well known that heating starch aqueous dispersions leads to a loss of both granular and crystalline structure. The behaviour of high amylose and waxy wheat starches during heating can be described as follows.

The behaviour of aqueous dispersions of Bulava starch at 56.7°C seems comparable to that of standard starch. At this temperature *A*-type starch granules start to swell. The microphotographs Fig. 5c and d suggest that amylose may come from the *B*-type granules, which undergo gelatinization earlier than *A*-type granules. At higher temperature (75°C), a more advanced swelling of starch granules can be observed. Some swollen granules changed their shape which resulted in release of amylose. This fact is probably connected with the first stage of starch gelatinization.

A rather different behaviour was observed in the case of Leona starch (Fig. 5a and b). The photos are in line with the poor amylose content of this starch. Some starch granules loose their granular shape at 62°C leaving ghost structures consisting of strongly hydrated amylopectin. Leona starch treated at higher temperature (75°C) (Fig. 5b) creates two different phases: a granular phase with swollen starch granules and a dispersed one with totally solubilised amylopectin (beige-bronze colour): starch granules retain their granular shape but seem to have a bronze envelope. This

'Leona', 1.5% amylose content, 56.7°C, magnification ×20

'Bulava', 39.5% amylose content, 56.7°C, magnification ×20



'Leona', 1.5% amylose content, 75.0°C, magnification ×20

'Bulava', 39.5% amylose content, 75.0°C, magnification ×20

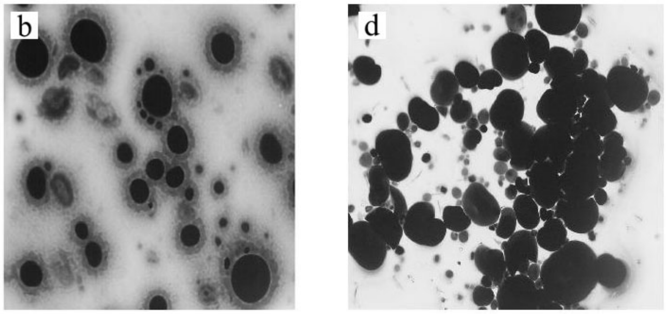


Fig. 5 Light microscopy micrographs of native starches extracted from different wheat varieties

fact can result from the 3D granule structure, namely from the different behaviour of outer and inner layers, the former undergoing faster hydration and solubilisation.

Original curves related to the melting of 0.3% aqueous starch dispersions (Fig. 6) show the typical endothermic transitions [15, 21, 22, 23–27]. The low-temperature endotherm is attributed to the melting of the crystalline lamellae, while the high-temperature peak is ascribed to the dissociation of the amylose-lipid complexes and/or the melting of single-helical V_h-type crystallites. Because of the low amylose content in starch from waxy wheat, the second transition is (almost) absent for this type of starch. All the thermodynamic melting parameters related to both crystalline lamellas and amylose-lipid complexes (Table 2), generally are in agreement with previously published [15, 21–23] data, although some differences can be noticed, which may be related to some influence of amylose on the structural organization of native granules. In particular, the decreasing trend of the melting enthalpy of starches observed with increasing (from 1.5 to 11.2%) amylose content (Table 2) can be due to the decreased crystallinity (Table 1). A further increase of the amylose content is not accompanied by changes of the values of both ΔH_{crl} and of crystallinity (Tables 1 and 2). A further finding is the decreasing trend of the melting temperature with increasing amylose content (Tables 1 and 2). According to the current interpre-

Table 2 Melting temperature ($T_{\mathrm{m\ crl}}$), melting enthalpy (ΔH_{crl}), vant Hoff's enthalpy ($\Delta H^{\mathrm{V_h}}$), heat capacity drop across the melting of crystalline lamellae (ΔC_{p}), and relevant hydration contribution ($\Delta C_{\mathrm{p\ hydr}}$), melting temperature ($T_{\mathrm{aml}}$) and melting enthalpy ($\Delta H_{\mathrm{alc}}$) of amylose-lipid complex in wheat starches with different amylose content

Wheat varieties	Amylose content/ %	$T_{\mathrm{m\ crl}}$/ K	ΔH_{crl}/ kJ mol^{-1}	$\Delta H^{\mathrm{V_h}}$/ kJ mol^{-1}	ΔC_{p}/ J mol^{-1} K^{-1}	$\Delta C_{\mathrm{p\ hydr}}$/ J mol^{-1} K^{-1}	T_{aml}/ K	ΔH_{alc}/ kJ mol^{-1}
Leona	1.5	336.6±0.2	2.8±0.2	37.3±0.4	37.0±2.5	24.5	362.9±0.8	0.23±0.05
Beseda	11.2	331.3±0.1	2.5±0.1	30.7±0.7	77.4±3.9	64.9	366.8±0.2	0.45±0.08
Moskovskya-39	21.0	331.4±0.1	2.4±0.2	30.3±1.1	54.2±7.8	41.7	367.2±0.2	0.55±0.11
Botovskaya	21.5	331.0±0.4	2.4±0.1	29.5±0.6	54.7±5.6	42.2	367.2±0.4	0.30±0.03
im. Rapoporta	26.0	330.5±0.1	2.3±0.1	31.2±0.9	37.5±3.8	45.0	363.2±0.4	0.30±0.05
Ritza	26.5	330.8±0.1	2.4±0.2	31.0±1.1	63.5±7.5	51.0	365.7±0.9	0.53±0.07
Bulava	39.5	329.7±0.1	2.5±0.1	28.6±2.0	19.0±8.0	6.5	366.8±0.1	0.42±0.04

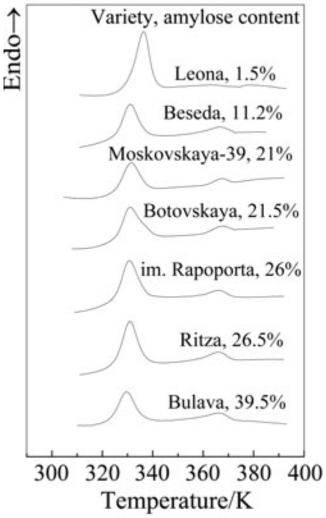


Fig. 6 DSC curves of native starches extracted from different wheat varieties

tation of the fusion of semi-crystalline synthetic polymers [35], a lower melting temperature can be related to a change of three parameters, namely: polymorphous structure of crystal, thickness and surface free energy of crystals.

According to the X-ray patterns (Fig. 4), the increase in the amylose content is not accompanied by any change of polymorphous structure, cooperative melting unit (ν), and thickness of crystalline lamellae (L_{crl}) (Table 3). It is worth noting that the calculated values of the ν and the L_{crl} are in agreement with published data relevant to other starches [21]. The data obtained (Tables 1 and 2, Fig. 4) can be interpreted according to the approach followed for semi-crystalline synthetic polymers [35] to suggest that a major reason for the observed change of the melting temperature may be related to a change of the surface free of crystals, γ_{i}. The γ_{i} value is mainly governed by the surface entropy, s_{i}, that is in turn related to concentration of structural (see above). Indeed, Table 3 data show that an increase in the amylose content is generally associated with an increase of s_{i}.

That defects exit within wheat starches can be confirmed through the estimation of the $\Delta C_{\mathrm{p}}^{\mathrm{hydr}}$ contribution to the overall heat capacity drop $\Delta C_{\mathrm{p}}^{\mathrm{exp}}$ across the fusion of crystalline lamellae [21, 23]. As previously shown [21, 23], $\Delta C_{\mathrm{p}}^{\mathrm{hydr}}$ for most starches, including wheat starches selected through usual breeding, does not exceed 18.5 J mol^{-1} K^{-1}. For waxy and normal maize, and for high amylose barley starches, $\Delta C_{\mathrm{p}}^{\mathrm{hydr}}$ is in the 27.1 to 56.1 J mol^{-1} K^{-1} range. Such differences, according to Yuryev *et al*. [21] and Matveev *et al*. [23], can be related to the higher content of defects, in particular amylose tie-chains, for maize and barley starches. As it can be seen from Table 2, the $\Delta C_{\mathrm{p}}^{\mathrm{hydr}}$ values for the investigated starches, except for the Bulava variety, are in the 24.5 to 64.5 J mol^{-1} K^{-1} range. This means that calculated values for wheat starches are comparable with those for maize and barley starches that host a high amount of defects. However the unusually low value of ΔC_p^{hydr} for starch from the Bulava variety demands some additional investigation.

In contrast to data for amylose-lipid complexes in maize and barley starches [19, 39, 40], the values of the melting temperature and enthalpy remain practically unchanged in wheat granules (Table 2), no matter the amylose content, with the exception of the data from waxy wheat starch. Taking into consideration that: (*i*) thermal stability of amylose lipid complexes depends on the nature of the lipid compound [41] and the crystalline state of complexes [22]; (*ii*) ΔH_{alc} is proportional to their content of granules, a reasonable conclusion may be that both the lipid compound and the crystalline state is the same in all these starches. A comparison between the values of ΔH_{alc} for wheat (Table 2), barley [39, 40] and maize [19, 40] starches suggests that the content of amylose-lipid complexes in wheat starches may be higher in the other starches.

Table 3 Surface free energy (γ_i), enthalpy (q_i) and entropy (s_i) of crystalline lamellae in wheat starches with different amylose content

Wheat varieties	Amylose content/%	γ_i/J cm$^{-2}\cdot10^7$	q_i/J cm$^{-2}\cdot10^7$	s_i/J cm^{-2} K$^{-1}\cdot10^7$
Leona	1.5	10.07	50.70	0.121
Beseda	11.2	11.86	55.84	0.133
Moskovskya-39	21.0	11.82	57.57	0.138
Botovskaya	21.5	11.96	57.57	0.138
im. Rapoporta	26.0	12.13	59.27	0.143
Ritza	26.5	12.03	57.57	0.138
Bulava	39.5	12.40	57.57	0.137

Conclusions

Different physical and chemical approaches aimed at determining the thermodynamic melting parameters coupled with methods for the investigation of the structure provide a reasonably exhaustive information about the structural organization of native granules at different molecular and supra-molecular levels.

The study of different structural levels of the macromolecular organization in wheat starches with different amylose content has shown that: (*i*) irrespective of the amylose content, the morphology (shape) of both large (*A*) and small (*B*) granules, as well as their size distribution, is practically not distinguishable from that of normal wheat starches; (*ii*) the content of the *A*-type polymorphous structure (formed double helixes with the degree of polymerization of 13.3) does not significantly change with the amylose content in the 11.2 to 39.5% range; (*iii*) irrespective of amylose content, the thickness of crystalline lamellae remains constant; (*iv*) crystalline and amorphous lamellas in native granules apparently contain defects.

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